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PROPERTIES OF NON-STOICHIOMETRIC METALLIC CARBIDES

by

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PROGRESS REPORT NO. 3

December 12, 1963

ADVANCED METALS RESEARCH CORPORATION

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SOMERVILLE 45, MASS.

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Headquarters
National Aeronautics and Space Administration
Washington 25, D. C.

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Properties of Non-Stoichiometric Metallic Carbides

I. Objectives of Work during Quarter

A. Prepare pure sintered carbide specimens having sufficient length to make thermal expansion and thermoelectric measurements.

B. Devise a means of attaching thermocouple leads to carbide specimens.

C. Construct a dialatometer suitable for making thermal expansion measurements on carbide specimens.

D. Obtain thermal expansion measurements on TiC from 0 to 1000°C.

II. Preparation of Specimens

Previous techniques of preparing dense, high purity, sintered, carbide specimens consisted of ball milling the hydride, graphite and paraffin mixtures, pressing into compacts one half inch in length, using a 3/8 cylindrical die, and firing at 1950°C for 3 hours. Longer lengths have not been possible using these techniques because of the bridging that occurs during the pressing operation. High pressures were required to obtain sufficient green strength to hold the compacts together while removing them from the die and loading into crucibles. It was decided to avoid this last step and prepare dies from pure spectroscopic graphite and fire die and all at the required temperature. The ball milled

mixture minus paraffin was loaded into prefired graphite dies 5/16 inch in diameter compacting with light pressure while taking extreme care to insure the uniformity of the compacting. The dies were then placed in the vacuum furnace and fired. This technique readily produced samples over two inches in length about 1/4 inch in diameter and over 85 percent dense. Two representative samples were analyzed for oxygen and nitrogen. The oxygen analyzed between 0.08 and 0.05 wt percent and the nitrogen below 0.01 wt percent. All the specimens used in subsequent measurements had well resolved diffraction peaks.

III. Lead Attachment

A number of experiments were performed to find the best method of attaching thermocouples to the carbide specimens. Attempts to weld the leads by providing external methods of heating were unsuccessful because of the very high melting point of the carbide. A technique which proved very satisfactory consisted of the following. The carbide specimen was mounted in a vacuum chamber in a thermally insulated holder with the thermocouple positioned adjacent to the spot where it was to be attached and then the specimen heated by electron bombardment. When the temperature of the specimen was about 100° above the melting temperature of the thermocouple material the couple was brought against the sample allowing it to melt and diffuse in a specified amount. Chromel-alumel couples were successfully attached in this way.

IV. Dialatometer Construction

A dialatometer was constructed to measure the thermal expansion

of the carbides over the temperature range of 0 - 1200°C. This device was designed so that it could be used in conjunction with the Brew high vacuum furnace and consisted of the following: A specimen holder, supporting tube and push rod all of quartz and a displacement transducer consisting of a differential transformer and associated circuitry. The transformer was placed in the vacuum chamber to eliminate the need of a vacuum seal between transducer and specimen. The temperature of the support for the transducer was maintained constant by water cooling. A sketch of this apparatus is shown in Figure 1.

Using the above apparatus a displacement of 1×10^{-5} inches could readily be detected. The temperature of the specimen was monitored with the aid of a thermocouple attached to the specimen. A very useful feature of the vacuum furnace is its small thermal mass enabling temperatures to be changed very rapidly which minimizes any error introduced by long term drifts in the expansion measurement.

D. Thermal Expansion Measurements

Sections showing the best uniformity were cut from the sintered bars and varied in length between 1-1/2 to two inches. The ends were cut parallel and polished on fine abrasive. Tantalum wire was used to secure the sample in the saddle provided for the specimen. Chromel-alumel couples attached directly to the specimens provided the means for measuring their temperature.

The dialatometer was calibrated with pure nickel using the following data:

	$\alpha \times 10^{-6}$	$a \times 10^{-9}$
0-350°C	12.54	8.75

This standard is not reliable above 350°C because of the magnetic transformation which occurs. The device will be further calibrated at higher temperatures using additional standards.

The expansion of the specimen was measured from room temperature to 1200°C. The carbide specimen used had nominal C/Ti ratios of 0.82, 0.84, 0.88, and 0.91, which cover the peak in the lattice parameter vs carbon composition curve. A plot of these results is shown in Figure 2.

Over the temperature range 0-1000° the expansion is best represented by a linear plot. The slope is greatest for the 0.82 composition and least for the 0.88 composition with the other two compositions lying in between. This leads to the following average values for the expansion coefficients $TiC_{0.82}$ α = 7.50 $TiC_{0.88}$ α = 7.00. A value for α reported in the literature is 7.42 (0-590°C) by Gangler[1] who prepared TiC samples by hot pressing.

The thermal expansion like other thermal properties, has its origin in the lattice vibration, the intensity of which increases as the temperature rises, thus the magnitude of the coefficient of thermal expansion of a particular body depends on its interatomic forces as well as on the structural arrangement. Since it has been suggested that the peak in lattice parameter versus carbon composition curve which occurs at a carbon content lower than the maximum value, is due to a weakening of these forces, one would expect a definite increase from the average expansion coefficient for carbon contents in the vicinity of the peak. This is certainly not observed at temperatures below 600°C. The variation in expansion at the highest temperatures is not in the direction

expected; however, additional data is needed to correctly establish the extent of the variation.

VI. Plans for Continuation of Work

Work will continue on those properties which are measurable on powder specimens. These include:

A. Additional thermal expansion measurements on TiC and ZrC.

B. Thermoelectric power measurements over a range of temperature on specimens of pressed powder.

References:

1. Gangler, J. J. , J. American Ceramic Society 33, 367 (1950)

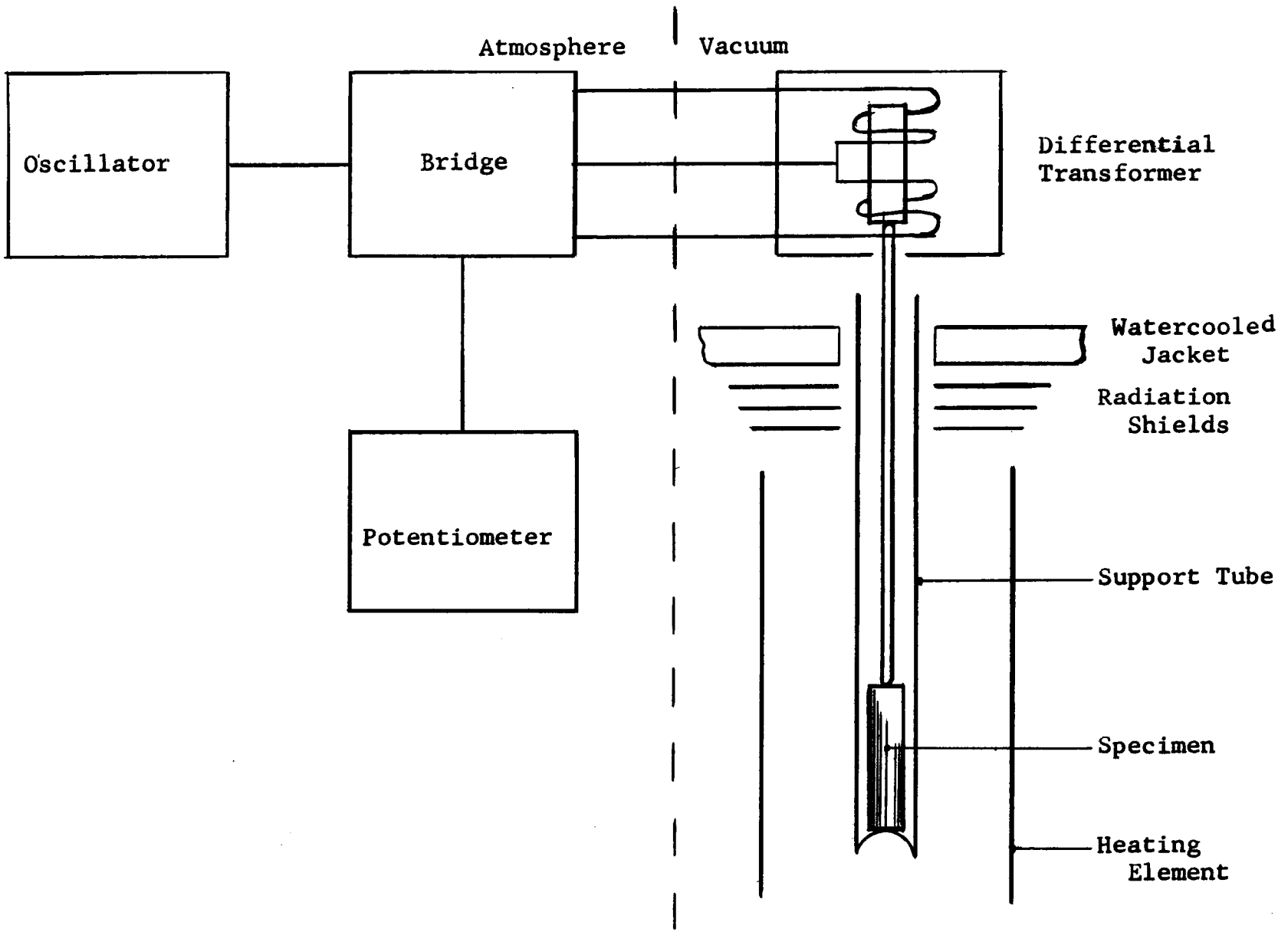

Figure 1. Dilatometer Schematic

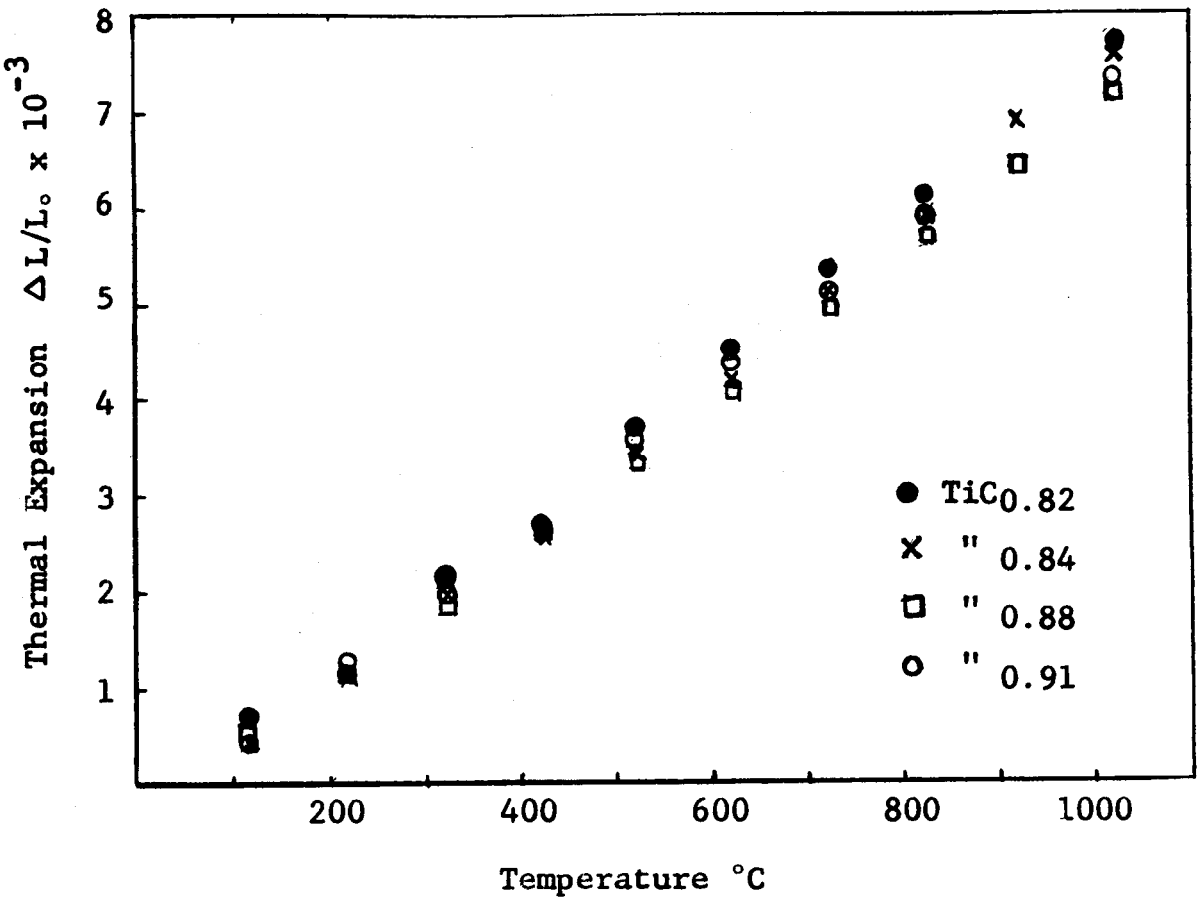

Figure 2. Thermal Expansion of TiC_x VS Temperature